

## COMPACTED EXPANDED GRAPHITE WITH A LOW THERMAL CONDUCTIVITY

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### Introduction

Expanded graphite (EG<sup>T</sup>), obtained by a thermal shock of expandable graphite (EG), is a low-density carbon material widely used as a base for sealing and fire-retardant materials. EG<sup>T</sup> is a promising material for high temperature (HT) insulation devices and heat-reflecting shields as well. Physicochemical properties of EG<sup>T</sup> and related materials, such as thermal and electrical conductivity, important for HT applications, strongly depend on the synthesis conditions of EG. While thermal characteristics of EG<sup>T</sup> obtained by the thermal shock of convenient graphite intercalation compounds (GICs) or their hydrolyzates (“poor compounds”) are well studied [1] the characteristics of EG<sup>T</sup> obtained by thermal shock of electrochemically synthesized EG are scarcely investigated. Since anodic polarization of graphite in 60% HNO<sub>3</sub> and consequent thermal shock result in intensive formation of structural defects in EG<sup>T</sup> [2] thermal conductivity of electrochemical samples can be greatly reduced in comparison with that of conventional samples.

Herein we report the synthesis of EG<sup>T</sup> through the thermal shock of electrochemically oxidized graphite and the investigation of thermal properties of compacted EG<sup>T</sup>.

### Experimental

Anodic polarization of natural purified graphite was carried at a stabilized current of 20 mA/cm<sup>2</sup> density with a total electrical charge transfer of 500-3000 C/g. 40%, 60% and 80% HNO<sub>3</sub> aqueous solutions were used as electrolytes. The resultant samples were then treated with water (20 ml/1 g of initial graphite) and dried in air at 60 °C for 2 hours to obtain EG samples. The EG samples are denoted as “acid concentration\_charge transfer”, i.e the sample synthesized in 60% HNO<sub>3</sub> with the 500 Q/g charge transfer is denoted as 60\_500. The reference “chemical” EG sample was obtained by water treatment of graphite nitrate of II stage. EG<sup>T</sup> samples were prepared by the thermal shock of the corresponding EG samples in air in the temperature range of 400-800 °C. Cylindrical samples (for thermal diffusivity measurements) of 0,2 g/cm<sup>3</sup> density ( $\rho$ ) and 12,7 mm diameter were then prepared by EG<sup>T</sup> uniaxial compression.

XRD experiments were carried on an ARL X'TRA diffractometer (CuK <sub>$\alpha$</sub>  radiation,  $\lambda = 1.5418 \text{ \AA}$ , Peltier detector)

in a 2 $\Theta$  range of 5-90 ° with the steps of 0,02°. Scanning electron microscopy (SEM) experiments were performed on a JEM-5510 instrument. Raman spectra were recorded at room temperature with a LabRam HR-800 spectrometer using the 488 nm mode of Ar<sup>+</sup> laser with a power of 0.01 mW. LFA 457 flash analyzer (NETZSCH) was utilized for thermal diffusivity ( $a$ ) measurements. Thermal conductivity  $\lambda$  was then calculated as  $\lambda = aC_p\rho$  with  $C_p$  value of pyrolytic graphite (0,711 J/gK).

### Results and Discussion

Graphite anodic oxidation in acid solutions is a complex process including a variety of processes: carbon macrocation formation, intercalation, GIC reoxidation, hydrolysis of *in situ* obtained GIC, carbon oxidation with the formation of covalent C-O bonds. The two latter processes are predominant in diluted solutions resulting in GO formation in 40\_3000 and in all the samples synthesized in 60% HNO<sub>3</sub> (Table 1). Hydrolysis doesn't influence the phase composition of these samples, just slight alteration of GO interlayer spacing occurs. GO content increases with increase of electrical charge transfer as follows from 100% reflections intensity ratio. Graphitic-like phase dG with an enlarged  $d_i$  value detected in all the samples polarized in 60% HNO<sub>3</sub> indicate the amorphization of the samples though the presence of crystalline graphitic reflections point to non-uniformity of

**Table 1. The XRD data for EG samples.**

Sample	EG Phase composition*	$I_{002G}/I_{002dG}/I_{001GO}$
graphite	G (3,35 Å, 70 nm)	na
“chemical” EG	G (3,35 Å, 55 nm) NG VIII ( $I_c=31,3 \text{ \AA}$ )	na
60_500	G (3,35 Å, 11nm) dG (3,50 Å, 11 nm) GO (13,47 Å, 17nm)	60/6/1
60_1000	G (3,35 Å, 11nm) dG (3,47 Å, 9 nm) GO (8,47 Å, 6 nm) GO (7,29 Å, 6 nm)	26/8/3
60_1500	G (3,35 Å, 7 nm) dG (3,44 Å, 8 nm) GO (13,15 Å, 13nm) GO (9,74 Å, 22 nm) GO (7,72 Å, 6 nm)	9/3/1
60_2000	G (3,35 Å, 7 nm) dG (3,49 Å, 7 nm) GO (8,41 Å, 6 nm) GO (6,65 Å, 6 nm)	9/5/4
60_3000	G (3,35 Å, 7 nm) dG (3,48 Å, 9 nm) GO (7,50 Å, 6 nm)	9/4/5
40_3000	G (3,35 Å, 24 nm) GO (7,87 Å, 5 nm)	7/-/1
80_3000	G (3,35 Å, 7 nm) GO (7,75 Å, 10 nm) GO (7,29 Å, 11 nm)	5/-/1

\*Indexes G, NG VIII ( $I_c=31,3 \text{ \AA}$ ), dG and GO correspond to graphite, graphite nitrate of VIII stage, graphitic-like carbon and graphite oxide respectively. The interlayer distance  $d_i$  and crystallite size along  $c$ -axis  $L_c$  values are listed in brackets.

oxidation mainly due to rather high current density. Graphite crystallite size is dramatically reduced being more significant for all the samples synthesized in 60 HNO<sub>3</sub> for 80\_3000 sample. The slight dependence of  $L_c$  size on the charge transfer for the samples synthesized in 60% HNO<sub>3</sub> imply that graphite  $L_c$  reduction accompanies the first stages of GO formation.

Thermal shock of synthesized samples results in the formation of worm-like EG<sup>T</sup> particles. EG<sup>T</sup> macrocharacteristics, i.e bulk density and carbon yield, are influenced by EG synthesis conditions (Table 2). The bulk density of the samples obtained at 400 and 600 °C from 60\_2000, 60\_3000 and 80\_3000 EG is as low as ~1 g/l and slightly depend on the expansion temperature implying GO thermal decomposition as the control factor for their expansion. The broad D- and G-lines of similar intensities are detected in the Raman spectra of these EG<sup>T</sup> samples which is indicative for nanocrystalline graphite and a high concentration of structural defects in the samples. On the contrary, the spectra of EG<sup>T</sup> from 600\_500 and “chemical” sample contain narrow G-line and are very close to natural graphite sample pointing to almost ideal graphitic microstructure.

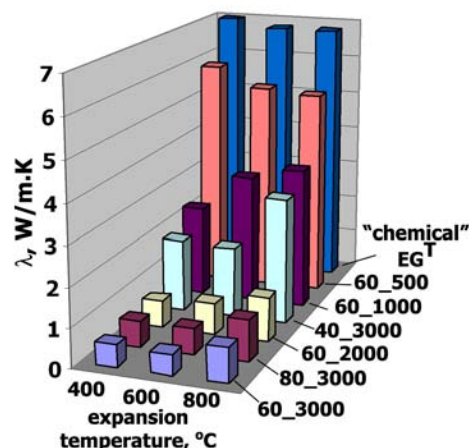
**Table 2. The EG<sup>T</sup> characteristics.**

Sample	Expansion temperature, °C	d, g/l	CY,%
60_500	400	3,2	84
	600	2	82
	800	1,7	70
60_1000	400	3,2	80
	600	1,8	75
	800	1,6	69
60_2000	400	1,1	68
	600	1,0	64
	800	1,0	60
60_3000	400	1,0	67
	600	0,9	64
	800	0,8	58
40_3000	400	2,5	80
	600	1,7	70
	800	1,6	65
80_3000	400	1,2	65
	600	1,0	64
	800	1,0	57

\*bd – bulk density=EG<sup>T</sup>mass/EG<sup>T</sup> volume  
CY – carbon yield=EGmass/EG<sup>T</sup>mass\*100%.

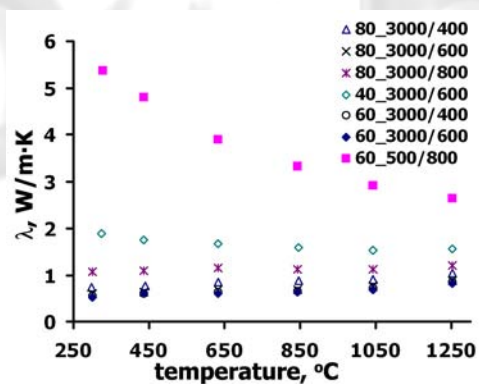
EG<sup>T</sup> samples were uniaxially compressed into the samples of 0,2 g/cm<sup>3</sup> density. The room temperature conductivity of the EG<sup>T</sup>s prepared from EG 60\_3000 at 400 and 600 °C (600\_3000/400 and 600\_3000/600 respectively) are as low as 0,55-0,6 W/m·K (Fig. 1). It's ~12 times lower than that of “chemical” sample which appears to be 7 W/m·K in agreement with Bonnissel [2]. Since EG<sup>T</sup> thermal conductivity density is known to be almost independent from the density in

the range of 0,1-1,5 g/cm<sup>3</sup> densities the obtained results are characteristic to flexible foils.



**Fig. 1** Room thermal conductivity of EG<sup>T</sup> samples versus expansion temperature.

The low thermal conductivity of compacted EG<sup>T</sup> from 60\_2000, 60\_3000 and 80\_3000 EG samples is attributed to their high dispersity and defectiveness, i.e. enormous quantity of boundaries and different defects are proposed to be responsible for phonon predominant boundary and defect scattering. Thermal conductivity temperature independence in the range of 298-1273 K for these EG<sup>T</sup> samples is congruent with the proposed suggestion (Fig. 2).



**Fig. 2** Thermal conductivity of EG<sup>T</sup> samples versus temperature.

The low thermal conductivity values were detected for EG<sup>T</sup> from EG synthesized in H<sub>2</sub>SO<sub>4</sub> solutions as well.

## Conclusions

Expanded graphite samples with the thermal conductivity of as low as 0,55-0,6 W/m·K were obtained by the thermal shock of electrochemically oxidized graphite in HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> solutions.

## References

- [1] Bonnissel M, Luo L, Tondeur D. Compacted exfoliated natural graphite as heat conduction medium. Carbon 39 2001; 2151-2161.
- [2] Afanasov IM, Shornikova ON, Kirilenko DA, Vlasov II, Zhang L, Verbeeck J, et al. Graphite structural transformations during intercalation and exfoliation. Carbon 48 2010; 1862-1865.